

X 1-4 6 8-12 15-17 22

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-031534

(43)Date of publication of application : 02.02.1999

(51)Int.Cl.

H01M 10/40

H01M 4/02

H01M 4/04

(21)Application number : 09-183960

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(22)Date of filing : 09.07.1997

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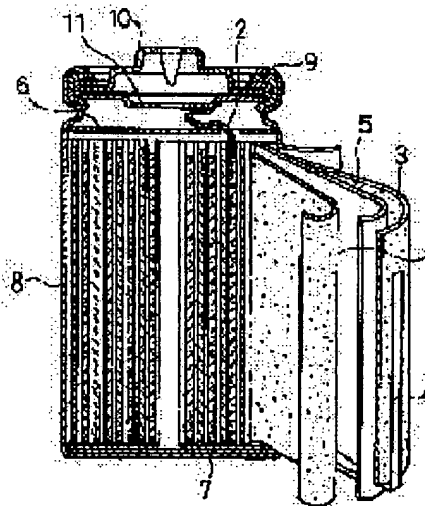
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY, AND MANUFACTURE OF ELECTRODE PLATE USED FOR THE NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery, in which deposition of metal lithium to a negative electrode at the time of charge is restricted and which has good charging and discharging cycle characteristic.

SOLUTION: This battery is provided with a positive electrode active material layer, which is mainly composed of Li-transition metal double oxide and which has continuous cavities, a negative electrode active material layer, which is mainly composed of graphite and which has continuous cavities, and a nonaqueous electrolyte, which is an organic solvent solution of lithium salt and which is filled in both the cavities. In this case, porosity of the positive electrode active material layer is set at 20-29 vol.%, and the porosity of the negative electrode active material layer is set at 30-45 vol.%.



LEGAL STATUS

[Date of request for examination]

22.05.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] The positive-active-material layer which has the opening which made Li-transition-metals multiple oxide the principal component, and continued. The negative-electrode active material layer which has the opening which made the graphite the principal component and continued. Nonaqueous electrolyte with which is an organic-solvent solution of lithium salt and both the aforementioned openings are filled up. It is the nonaqueous electrolyte rechargeable battery equipped with the above, and the voidage of the aforementioned positive-active-material layer is 20 - 29vol%, and it is characterized by the voidage of the aforementioned negative-electrode active material layer being 30 - 45vol%.

[Claim 2] In the manufacture method of the electrode board used for a nonaqueous electrolyte rechargeable battery according to claim 1 It applies to a positive-electrode charge collector sheet so that a solvent may be made to suspend a positive active material, it may be made the shape of a paste and the voidage after an application and dryness may become 60 - 70vol%. After drying, roll out and voidage of a positive-active-material layer is made into 20 - 29vol%. The manufacture method of the electrode board characterized by rolling out and making voidage of a negative-electrode active material layer into 30 - 45vol% after applying and drying on a negative-electrode charge collector sheet so that a solvent may be made to suspend a negative-electrode active material, it may be made the shape of a paste and the voidage after an application and dryness may become 50 - 65vol%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of the electrode board used for nonaqueous electrolyte rechargeable batteries, such as a lithium secondary battery, and this.

[0002]

[Description of the Prior Art] In recent years, portable-izing of consumer electronics and cordless-ization are progressing quickly. Small [which bears the power supply for a drive along with this], and the requests to the rechargeable battery which is lightweight and has high-energy density are mounting. The expectation of the nonaqueous electrolyte rechargeable battery from such a viewpoint, especially a lithium secondary battery is great as a rechargeable battery which especially has a high voltage and high-energy density, and development is hurried.

[0003] Manganese dioxide, a vanadium pentoxide, 2 titanium sulfides, etc. were used for the positive active material of the conventional lithium secondary battery. The lithium secondary battery consisted of a positive electrode using these positive active materials, a negative electrode using Metal Li, and the organic electrolytic solution. However, in the rechargeable battery which used Metal Li for the negative electrode, there is a problem of the metal Li which deposits on a negative electrode at the time of charge growing in the shape of a dendrite, and breaking through separator, and causing an internal short circuit between positive electrodes, or causing side reaction between the electrolytic solutions. since growth of the dendrite of the aforementioned metal Li will grow more greatly if it charges with big current, and if charge and discharge are repeated, high-speed charge is difficult for it -- it carries out a charge-and-discharge cycle life is short -- carrying out -- the further aforementioned interior -- simplistic -- it has also been a serious obstacle to utilization that there is danger, such as to result in more intense generation of heat and a more intense liquid spill

[0004] LiCoO₂ which can emit Li ion in reversible as a positive electrode using the negative-electrode active material which recently makes a principal component the carbon material of the graphite system which can intercalate Li in reversible, not using Metal Li as a negative electrode etc. -- the lithium secondary battery using the positive active material which makes Li-transition-metals multiple oxide a principal component is proposed as what aims at solution of the above-mentioned problem

[0005]

[Problem(s) to be Solved by the Invention] However, also in the lithium secondary battery which used the above-mentioned Li-transition-metals multiple oxide for the positive active material, and used the carbon material of a graphite system for the negative-electrode active material, it became clear that it is not necessarily enough to suppress a deposit of the metal Li to the negative-electrode top at the time of charge, and that the acquired charge-and-discharge cycle property of a lithium secondary battery is greatly dependent on the manufacture conditions of a positive-electrode board and a negative-electrode board as a result of examination by this invention person.

[0006] this invention aims at offering the manufacture method of the electrode board which suppresses a deposit of the metal Li to the negative electrode at the time of charge, and is used for a nonaqueous electrolyte rechargeable battery and this with a sufficient charge-and-discharge cycle property in view of the above-mentioned problem.

[0007]

[Means for Solving the Problem] The positive-active-material layer which has the opening which made Li-transition-metals multiple oxide the principal component, and continued in order that this invention may attain the above-mentioned purpose, In the nonaqueous electrolyte rechargeable battery equipped with the negative-electrode active material layer which has the opening which made the graphite the principal component and continued, and the nonaqueous electrolyte with which are an organic-solvent solution of lithium salt and both the aforementioned openings are filled up The voidage of the aforementioned positive-active-material layer is 20 - 29vol%, and it is characterized by the voidage of the aforementioned negative-electrode active material layer being 30 - 45vol%.

[0008] Since according to the nonaqueous electrolyte rechargeable battery of this invention it constitutes so that the voidage of a negative-electrode active material layer may become larger than that of a positive active material, the rate of volume of the electrolytic solution in a negative-electrode active material layer becomes larger than it in a positive active material, and Li mobility of ion in a negative-electrode active material layer becomes large from it in a positive-active-material layer. Therefore, since Li ion supplied into the electrolytic solution from a positive-electrode side into the negative-electrode active material layer at the time of charge is intercalated in a negative-electrode active material smoothly [it is reasonable and], it can stop that Metal Li deposits on the part of a negative electrode. And as shown in drawing 2 and drawing 4 , the range of the voidage of a positive-active-material layer is 20 - 29vol%, and the voidage of a negative-electrode active material layer is kept proper between a positive electrode and a negative electrode in the range of 30 - 45vol%, and the balance of each amount of active materials and the size relation of Li mobility of ion in each active material layer can obtain a nonaqueous electrolyte rechargeable battery with a sufficient charge-and-discharge cycle property.

[0009] Since the filling factor of a positive active material will become small if the voidage of a positive-active-material layer exceeds 29vol(s)% preferably since the internal resistance at the time of electric discharge increases as a result of the rate of volume of the electrolytic solution in a positive-active-material layer becoming small and Li mobility of ion in a positive-active-material layer falling, if the voidage of a positive-active-material layer is not filled to 20vol(s)%, and the cell capacity per unit volume falls, it is not desirable. Moreover, if the voidage of a negative-electrode active material layer is not filled to 30vol(s)%, the rate of volume of the electrolytic solution in a negative-electrode active material layer will become small. If the voidage of a negative-electrode active material layer exceeds

45vol(s)% preferably in order for Metal Li to deposit on the part of a negative electrode and to grow up in the shape of a dendrite as a result of the fall of Li mobility of ion in a negative-electrode active material layer. Since the filling factor of a negative-electrode active material becomes small, the electric conductivity in a negative-electrode active material falls, and the cell capacity per unit volume falls, it is not desirable.

[0010] In the manufacture method of the electrode board used for the aforementioned nonaqueous electrolyte rechargeable battery, a solvent is made to suspend a positive active material and it is made the shape of a paste. An application, It applies to a positive-electrode charge collector sheet so that the voidage after dryness may become 60 - 70vol%. After drying, roll out and voidage of a positive-active-material layer is made into 20 - 29vol%. If it rolls out and voidage of a negative-electrode active material layer is made into 30 - 45vol% after applying and drying on a negative-electrode charge collector sheet so that a solvent may be made to suspend a negative-electrode active material, it may be made the shape of a paste and the voidage after an application and dryness may become 50 - 65vol%. As an application, dryness, and rolling can be manufactured reasonable with a long sheet convenient for the consistent automation and the electrode board used for the aforementioned nonaqueous electrolyte rechargeable battery is shown in drawing 3 and drawing 5. The range of the voidage after the application of a positive active material and dryness is 60 - 70vol%, and the voidage after the application of a negative-electrode active material and dryness can obtain a nonaqueous electrolyte rechargeable battery with a sufficient charge-and-discharge cycle property in the range of 50 - 65vol%.

[0011] If the voidage after the application of a positive active material and dryness is not filled to 60vol(s)%, the subsequent rate of rolling will become small. If the voidage after the application of a positive active material and dryness exceeds 70vol(s)% preferably since the internal resistance at the time of electric discharge increases as a result of the electric contact degree of a positive active material and a positive-electrode board decreasing and the electric conductivity in a positive-active-material layer falling. It is not desirable, in order that a big cavity may be generated unevenly and the distribution nonuniformity of a positive active material may remain also with subsequent rolling into a positive-active-material layer. Moreover, if the voidage after the application of a negative-electrode active material and dryness is not filled to 50vol(s)%. Since the subsequent rate of rolling becomes small, the electric contact degree of a negative-electrode active material and a negative-electrode board decreases and the electric conductivity in a negative-electrode active material layer falls, if the voidage after the application of a negative-electrode active material and dryness exceeds 65vol(s)% preferably. As a result of the subsequent rate of rolling becoming large, the BESARU side of the graphite of the principal component of a negative-electrode active material carrying out orientation in parallel with a negative-electrode plate surface and Li mobility of ion in a negative-electrode active material layer falling, since Metal Li deposits on the part of a negative electrode at the time of charge, it is not desirable.

[0012]

[Embodiments of the Invention] The operation gestalt of this invention is explained below based on a drawing.

[0013] 1 operation gestalt of the nonaqueous electrolyte rechargeable battery of this invention is a cylindrical lithium secondary battery as shown in drawing 1, and consists of a group of electrode, the electrolytic solution, and a cell case where these are held.

[0014] A group of electrode consists of the separator 5, the positive-electrode lead 2, the negative-electrode lead 4, the up electric insulating plate 6, and the lower electric insulating plate 7 of the shape of a sheet which insulates between the sheet-like positive-electrode board 1, the sheet-like negative-electrode board 3, and the positive-electrode board 1 and the negative-electrode board 3. The positive-electrode board 1 carries out application formation so that the voidage may become 20 - 29vol% about a positive-active-material layer at both sides of an aluminum foil. The negative-electrode board 3 carries out application formation so that the voidage may become 30 - 45vol% about a negative-electrode active material layer at both sides of copper foil. These positive-electrodes board 1 and the negative-electrode board 3 pile up through the separator 5 made from a porosity polypropylene film, are wound in the shape of a whorl, and are just held in the cylindrical cell case.

[0015] The electrolytic solution becomes the isochore product mixed solvent of an ethylene carbonate and a propylene carbonate from the nonaqueous electrolyte which dissolved the lithium perchlorate in the concentration of 1 mol/liter. This nonaqueous electrolyte is held in a cell case, and it fills up with it also into the opening followed in the positive-active-material layer and the negative-electrode active material layer, and it bears movement of Li ion between the positive-electrode board 1 which lets the micropore of the porosity separator 5 pass, and the negative-electrode board 3 in a cell reaction.

[0016] A cell case consists of an insulating gasket 9 which insulates and carries out the gas seal of between the case main parts 8 used as the case main part 8 which carried out deep-drawing fabrication and obtained the stainless steel plate of organic-proof electrolytic-solution nature, the obturation board 10 which formed the relief valve 11, the obturation board 10 used as a positive-electrode external terminal, and a negative-electrode external terminal.

[0017] 1 operation gestalt of the manufacture method of the electrode board used for the nonaqueous electrolyte rechargeable battery of the aforementioned this invention is explained below.

[0018] As shown in Table 1, the positive-electrode board 1 controlled manufacture conditions variously, and obtained 11 kinds of things of positive-electrode board sample A-L to which the voidage after the voidage of an active material layer and the application of an active material, and dryness was changed. Specifically, it is Li₂CO₃ first, CoCO₃ LiCoO₂ which carried out 10hr baking and which was obtained at 900 degrees C after mixing Powder 90wt%, acetylene black 3wt%, and fluoro-resin system binder 7wt% were mixed, mixture was obtained, subsequently to carboxyl methyl-cellulose 1wt% solution this mixture was made to suspend, and the positive-active-material paste of various concentration (water content) was obtained. And to both sides of aluminum foil with a thickness of 0.02mm, it applied to various thickness, this positive-active-material paste was dried, and the positive-electrode application layer of the various voidage according to the used concentration of a positive-active-material paste was obtained. At the last, they were rolled out so that it might become 0.18mm in thickness, and it judged at it, and positive-electrode board sample A-L with a width of face [of 40mm] and a length of 350mm was obtained at it. In addition, although the appearance density and application thickness corresponding to voidage are written together in Table 1, in an actual manufacturing process, this appearance density and application thickness are more convenient for condition management.

[0019] As shown in Table 2, the negative-electrode board 3 controlled manufacture conditions variously, and obtained 12 kinds of things of negative-electrode board sample M-Y to which the voidage after the voidage of an active material layer and the application of an active material, and dryness was changed. Specifically, after grinding the corks which come to carry out the high-temperature carbonization of the coal first so that a mean particle diameter may be set to 6.0 micrometers with a jet mill, they were calcinated and graphitized at 2800 degrees C. The specific surface area of the obtained graphite powder was 5.0m² / g. This graphite-powder 90wt% and fluoro-resin system binder 10wt% were mixed, mixture was obtained, subsequently to carboxyl methyl-cellulose 1wt% solution this mixture was made to

*Li₂CO₃
reagent
only*

suspend, and the negative-electrode active material paste of various concentration (water content) was obtained. And the negative-electrode application layer of the various voidage according to the concentration of the negative-electrode active material paste which applied this negative-electrode active material paste to both sides of copper foil with a thickness of 0.02mm, and dried and used it for various thickness at them was obtained. At the last, they were rolled out so that it might become 0.19mm in thickness, and it judged at it, and negative-electrode board sample M-Y with a width of face [of 40mm] and a length of 420mm was obtained at it. Also to this table 2, the appearance density and application thickness corresponding to voidage were written together, and the facilities of actual condition management were given to it.

[0020]

[Table 1]

positive electrode

正極板試料	単位	A	B	C	D	E	F	G	H	J	K	L
ペースト含水率	wt%	63	57	50	44	38	50					
活物質塗布厚み	(mm)	0.55	0.47	0.41	0.36	0.32	0.38	0.39	0.41	0.43	0.44	0.45
活物質の塗布乾燥後の空隙率	vol%	75	70	65	60	55	65					
(みかけ密度)	(g/cm ³)	1.2	1.4	1.6	1.8	2.0	1.6					
活物質層の厚み	(mm)	0.16										
活物質層の空隙率	vol%	26					35	32	29	23	20	17
(みかけ密度)	(g/cm ³)	3.5					3.2	3.3	3.4	3.6	3.7	3.8
圧延率	%	70	64	59	53	47	56	57	58	61	62	63

[0021]

[Table 2]

negative electrode

50% porosity? .21 mm?

負極板試料	単位	M	N	P	Q	R	S	T	U	V	W	X	Y
ペースト含水率	wt%	70	66	60	55	50	43	35	50				
活物質塗布厚み	(mm)	0.39	0.33	0.29	0.25	0.23	0.21	0.19	0.21	0.23	0.27	0.29	0.31
活物質の塗布乾燥後の空隙率	vol%	75	70	65	60	55	50	45	55				
(みかけ密度)	(g/cm ³)	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.0				
活物質層の厚み	(mm)	0.17											
活物質層の空隙率	vol%	45							50	40	35	30	25
(みかけ密度)	(g/cm ³)	1.2							1.1	1.3	1.4	1.5	1.6
圧延率	%	54	45	36	27	18	9	0	10	21	31	37	41

[0022] Combining various the aforementioned positive-electrode board sample A-L and negative-electrode board sample M-Y, it incorporated in the cell case with winding, a diameter [of 17mm], and a height of 50mm in the shape of a whorl through the separator made from a porosity polypropylene film with the thickness of 0.025mm, a width of face [of 46mm], and a length of 900mm, and was filled up with the aforementioned nonaqueous electrolyte. In this way, the lithium secondary battery used combining various positive-electrode boards 1 and negative-electrode boards 3 by manufacture conditions was obtained. The evaluation result of the charge-and-discharge cycle property of the obtained lithium secondary battery is shown in drawing 2 - drawing 6.

[0023] The one evaluation method of a charge-and-discharge cycle property sets the initial charging current to 500mA under the environmental temperature of 20 degrees C. After charging for 2 hours, restricting charge upper limit voltage to 4.2V and leaving it for 30 minutes It was made to discharge until final voltage was set to 3V with 720mA fixed current, the service capacity after repeating this charge-and-discharge cycle 500 times was measured, and as shown in drawing 2 - drawing 5, the variable of each manufacture conditions

was taken and plotted on the horizontal axis.

[0024] Drawing 2 was drawing showing the relation between the voidage of a positive-active-material layer, and a charge-and-discharge cycle property, all the voidage after the application of the positive active material before rolling and dryness considered as 65vol(s)%, and all the negative-electrode boards put together were made into the negative-electrode board sample R. As shown in drawing 2, in the range of 20 - 29vol% (positive-electrode board samples H, C, J, and K), the good charge-and-discharge cycle property was acquired for the voidage of a positive-active-material layer.

[0025] Drawing 3 was drawing showing the relation between the voidage after the application of a positive active material, and dryness, and a charge-and-discharge cycle property, all the voidage of the positive-active-material layer after rolling considered as 26vol(s)%, and all the negative-electrode boards put together were made into the negative-electrode board sample R. As shown in drawing 3, in the range of 60 - 75vol% (positive-electrode board samples B, C, and D), the good charge-and-discharge cycle property was acquired for the voidage after the application of a positive active material, and dryness.

[0026] Drawing 4 was drawing showing the relation between the voidage of a negative-electrode active material layer, and a charge-and-discharge cycle property, all the voidage after the application of the negative-electrode active material before rolling and dryness considered as 55vol(s)%, and all the positive-electrode boards put together were made into the positive-electrode board sample C. As shown in drawing 4, in the range of 30 - 45vol% (negative-electrode board samples R, V, W, and X), the good charge-and-discharge cycle property was acquired for the voidage of a negative-electrode active material layer.

[0027] Drawing 5 was drawing showing the relation between the voidage after the application of a negative-electrode active material, and dryness, and a charge-and-discharge cycle property, all the voidage of the negative-electrode active material layer after rolling considered as 45vol(s)%, and all the positive-electrode boards put together were made into the positive-electrode board sample C. As shown in drawing 5, in the range of 50 - 65vol% (negative-electrode board samples P, Q, R, and S), the good charge-and-discharge cycle property was acquired for the voidage after the application of a negative-electrode active material, and dryness. About each lithium secondary battery by four kinds of typical combination, another evaluation method of a charge-and-discharge cycle property repeated the same charge-and-discharge cycle conditions as the above, measured service capacity for every cycle, and as shown in drawing 6, it took and plotted the number of cycles on the horizontal axis. Specifically, it evaluated about the combination of four kinds of positive-electrode board sample-negative-electrode board samples, i.e., J-V, J-Y, F-V, and F-Y. As shown in drawing 6, early service capacity is large, the fall of the service capacity to the increase in the number of cycles is small, namely, the thing using the big negative-electrode board sample V of voidage (voidage 40vol%) and the small positive-electrode board sample J of voidage (voidage 23vol%) is understood that a charge-and-discharge cycle property is good. Early service capacity does not have [the thing using the desirable or large, big positive-electrode board sample F of voidage (voidage 35vol%)] the small desirable fall of service capacity [as opposed to the increase in the number of cycles in the thing using the small negative-electrode board sample Y of voidage (voidage 25vol%)].

[0028] These things and the result of aforementioned drawing 2 and drawing 4 show that the voidage of the active material layer of a negative-electrode board is large, and a charge-and-discharge cycle property has a good thing with the small voidage of the active material layer of a positive-electrode board. Of course, if the voidage of the active material layer of a negative-electrode board becomes extremely large, since the filling factor of a negative-electrode active material becomes small, the electric electric conductivity in a negative-electrode active material will fall and the cell capacity per unit volume of a cell will fall, it is not desirable. Moreover, if the voidage of the active material layer of a positive-electrode board becomes extremely small, since Li mobility of ion in a positive-active-material layer will fall, it is not desirable.

[0029] Moreover, it turns out that a good charge-and-discharge cycle property is acquired from the result of aforementioned drawing 3 and drawing 5 by rolling out the suitable rate of rolling for a positive-electrode board and each negative-electrode board. LiCoO₂ which is not especially good in itself as for electric electric conductivity the positive active material which makes powder a principal component -- electric conduction material -- adding -- a certain grade -- by performing big rolling, sufficient electric electric conductivity is given for the first time, and a good charge-and-discharge cycle property is acquired

[0030]

[Effect of the Invention] Since according to the nonaqueous electrolyte rechargeable battery of this invention it constitutes so that the voidage of a negative-electrode active material layer may become larger than that of a positive active material, the rate of volume of the electrolytic solution in a negative-electrode active material layer becomes larger than it in a positive active material, and Li mobility of ion in a negative-electrode active material layer becomes large from it in a positive-active-material layer. Therefore, since Li ion supplied into the electrolytic solution from a positive-electrode side into the negative-electrode active material layer at the time of charge is intercalated in a negative-electrode active material smoothly [it is reasonable and], it can stop that Metal Li deposits on the part of a negative electrode. And the range of the voidage of a positive-active-material layer is 20 - 29vol%, and the voidage of a negative-electrode active material layer is kept proper between a positive electrode and a negative electrode in the range of 30 - 45vol%, and the balance of each amount of active materials and the size relation of Li mobility of ion in each active material layer can obtain a nonaqueous electrolyte rechargeable battery with a sufficient charge-and-discharge cycle property.

[Translation done.]